

PHOTOCHEMISTRY OF PYRUVIC ACID IN WATER AND ICE

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Marcelo Ioel Guzmán

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ABSTRACT

The 321 nm band photodecarboxylation of aqueous pyruvic acid, PA, solutions was studied over the range $5 \leq [\text{PA}] \leq 100$ mM. Immediate and delayed CO_2 production stages were detected using TEMPO as a scavenger. During the irradiation of frozen aqueous solutions of PA, CO_2 evolution occurs; however, additional CO_2 is released in the absence of light. The release rate under dark conditions was found to be first order in $[\text{CO}_2]$ with an activation energy $E_a \sim 22 \text{ kJ mol}^{-1}$ at $T < 268 \text{ K}$. Photodecarboxylation rates of anoxic aqueous PA solutions decreased two-fold in the frozen state at 253 K relative to the liquid state at 293 K. In contrast, there was no post-illumination emission of CO_2 during the photodecomposition of benzoylformic acid in frozen solutions.

Magic angle spinning ^1H -NMR measurements were made to determine the hydration state of aqueous PA between the carbonyl and its hydrated gem-diol counterpart, PAH. In the frozen state, the fraction of the photoactive carbonyl-form of PA, approaches $\sim 20\%$ at temperatures below 263 K, regardless of the initial PA concentration over the range $0.1 \text{ M} \leq [\text{PA}] \leq 4.6 \text{ M}$. Calculations show that ~ 4 water molecules are involved in the hydration of PA in ice at 243 K. Pyruvic acid is cooperatively hydrated while dissolved, or partitioned into viscous aqueous microfluids often called quasi liquid layers (QLL) down to the glass transition.

Electron magnetic resonance measurements of frozen aqueous solutions of PA that were irradiated at $\lambda = 313 \text{ nm}$ and at $T = 77 \text{ K}$ were determined to be distant triplet radical pairs separated by approximately 0.9 nm. These triplet pairs are formed by photoinduced electron transfer between a triplet excited state of PA and corresponding ground state of PA

to produce $^3[\text{PA}^+ \cdot \text{PA}^- \cdot]$. The subsequent deprotonation of $\text{PA}^+ \cdot$ into an acylcarbonyloxy radical which undergoes an ultrafast decarboxylation, accounts for the post-illuminated CO_2 . Liquid chromatography with UV and ESI-MS detection combined with ^{13}C -isotope labeling techniques were used to identify products. The protonated radical anion $\text{PA}^- \cdot$ (i.e., a ketyl-radical) self-reacts to form 2,3-dimethyltartaric acid. Another pathway involving reaction of the ketyl radical with ground-state PA forms an unstable β -keto dicarboxylic acid, which undergoes CO_2 elimination to produce 2-(3-oxobutan-2-yl)-2-hydroxypropanoic acid.

In conclusion, the possibility of photolysis in ice core records due to penetrating Cerenkov radiation derived from cosmic rays is explored. Potential impacts of the photolysis of organic matter trapped in ice with the subsequent release of CO and CO_2 over the last two millennia is analyzed.

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